Ionothermal synthesis of 3d–4f and 4f layered anionic metal–organic frameworks†

Wen-Xian Chen, Yan-Ping Ren,* La-Sheng Long,* Rong-Bin Huang and Lan-Sun Zheng

Received 22nd January 2009, Accepted 24th April 2009
First published as an Advance Article on the web 21st May 2009
DOI: 10.1039/b901404g

A La(III)–Co(II) heterometallic framework and a La(III)-based anionic layered architecture were prepared under ionothermal conditions.

Ionic liquids (ILs), a class of organic solvents, have received much attention recently due to their peculiar properties, including unusually low melting points, nonvolatility, nonflammability, thermally stability, recycle and versatile ability to dissolve many substances.[1,2] Normally, ILs are highly studied in separations, electrochemistry, lubrications, life sciences, and catalytically active solvents for synthetic chemistry, *etc*.[3] Recently, based on their unique properties, ILs have been explored and utilized in the areas of zeotypes preparation and synthetic coordination chemistry.[4,5] Distinguishing from traditional hydro/solvothermal syntheses which are frequently strategies to construction of coordination polymers,[6,7] ionothermal synthesis is of particular interest, in which ionic liquids participate as both solvent and structure-directing agent, resulting in interesting anionic metal–organic frameworks.[8] It is worth noting that ionothermal synthesis of metal–organic frameworks, while very common in transition-metal-based coordination polymers,[9] is almost absent in the construction of 3d–4f or 4f coordination structures up to date, despite the effort made in this field.[10] We report the ionothermal synthesis of two lanthanide-based frameworks, namely, $[La_2Co(mipt)_2(CH_3COO)_2(CH_3SO_3)_4][EMIm]_2$ (**1**) and [La(nip)BrCl][EMIm] (**2**).

The one-pot reaction of 5-methylisophthalic acid (H_2mipt), $LaCl_3\cdot nH_2O$ and $Co(OOCCH_3)_2\cdot 4H_2O$ in ionic liquid 1-ethyl-3-methyl imidazolium methanesulfonate (EMIm-MSul) resulted in pink crystals of **1**.‡ Fig. 1a shows the coordination environment of La(III) and Co(II) in **1**. The structure of **1**§ features a layered La(III)–Co(II) heterometallic anionic open framework which is made up of infinite La(III)–Co(II) chains connected by mipt ligands. The coordination environment around the Co(II) ion, located in hexa-coordinated octahedron geometry, is coordinated by two mipt ligands, two CH_3COO^- anions and two $CH_3SO_3^-$ anions. The Co–O distances, ranging from 2.067(4) to 2.149(4) Å, are in agreement with those observed for the hexa-coordinated Co atom in carboxylate complexes.[11] In **1**, the central La(III) ion is ligated by three monodentate $CH_3SO_3^-$ anions, one monodentate CH_3COO^- anion, one bidentate CH_3COO^- anion, one bidentate carboxylate and one monodentate carboxylate, respectively, from two different mipt ligands in a capped square antiprism coordination geometry. The La–O distances range from 2.421(4) to 2.706(4) Å, compared to those of 2.398(3)–2.678(3) Å in the nona-coordinated La(III)-complex.[12] Two La(III) centers linked, respectively, through a pair of CH_3COO^- anions and $CH_3SO_3^-$ anions, result in a dinuclear unit. The connection of adjacent dinuclear units through CoO_6 entity generates a 1D La(III)–Co(II) heterometallic chain as shown in Fig. 2a. The mipt ligand bridges adjacent chains through its one carboxylate coordinating with one La(III) ion from one neighboring chain in chelating mode, and another carboxylate bridged one La(III) and one Co(II) from another neighboring chain in *syn–syn* bridging mode, leading to a 2D anionic network. EMIm cations acting as guests and encounter ions, located in the hydrophobic cavity of **1** as illustrated in Fig. 2b, while the anionic component $CH_3SO_3^-$ ions of the ionic liquid are coordinated with the La(III) ion in **1**.

Mixing 5-nitroisophthalic acid (H_2nip), $LaCl_3\cdot nH_2O$ in ionic liquid 1-ethyl-3-methyl imidazolium bromide (EMIm-Br) through ionothermal reaction results in colorless needle crystals of **2**.‡

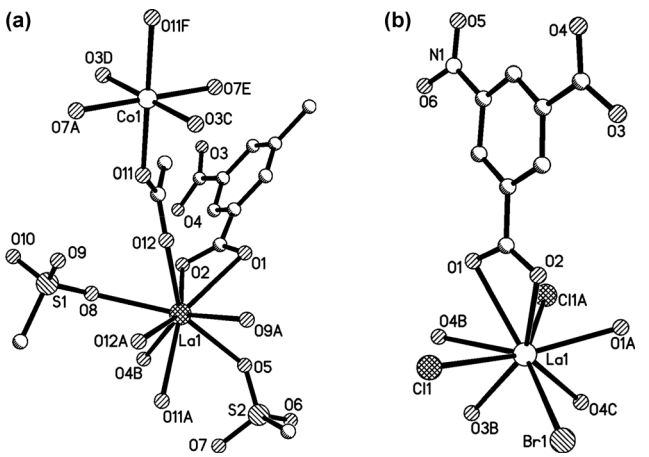

Fig. 1 ORTEP plot showing (a) the coordination environment of La(III) and Co(II) ions in **1**. Symmetry codes: A $-x+1, -y+2, -z+1$; B $-x+1, -y+2, -z+2$; C $x, y, z-1$; D $-x, -y+2, -z+2$; E $x-1, y, z$; F $-x, -y+2, -z+1$. (b) The coordination environment of La(III) ion in **2**. Symmetry codes: A $-x+1/2, y, z+1/2$; B $x, y-1, z$; C $-x+1/2, y-1, z+1/2$.

State Key Laboratory of Physical Chemistry of Solid Surface, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China. E-mail: lslong@xmu.edu.cn; ypren@xmu.edu.cn; Fax: +86 592 218 3047

† Electronic supplementary information (ESI) available: TG analysis for compounds **1** and **2** (Fig. S1–S2); IR spectra for compounds **1** and **2** (Fig. S3–S4); . CCDC reference numbers 717557 and 717558. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901404g

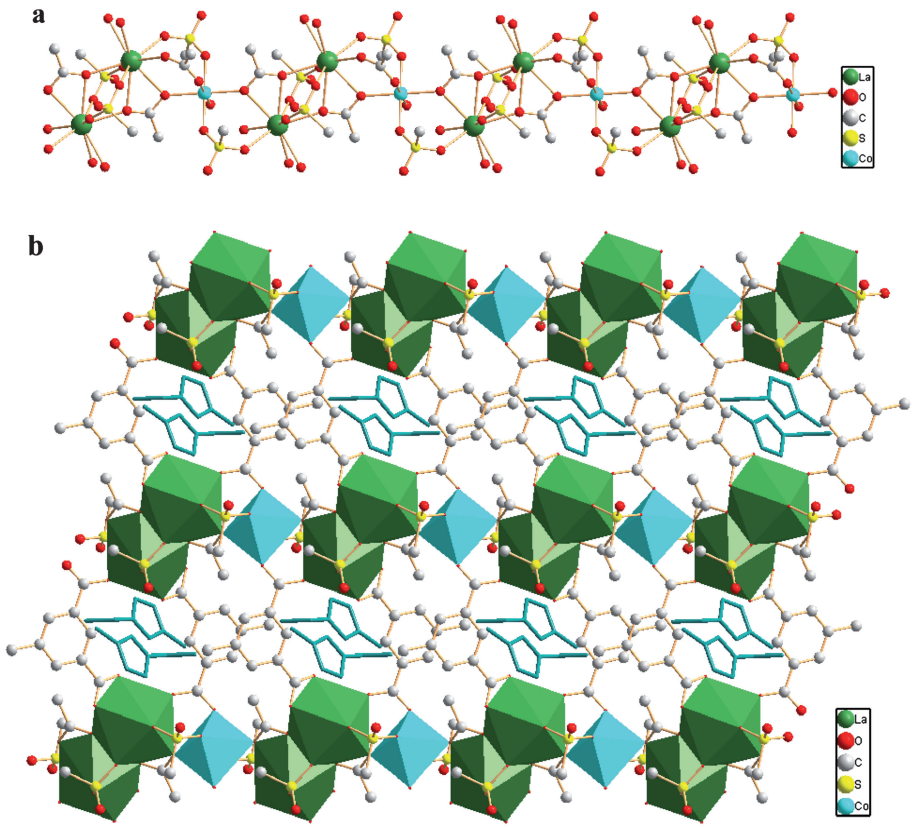

Fig. 2 (a) Ball and stick plot showing the 1D chain structure in **1**. (b) Polyhedral view of the 2D structure of **1**.

Single-crystal analysis reveals that **2** is crystallized in the orthorhombic system, space group $Pca2_1$.§ Fig. 1b shows the coordination environment of La(III) in **2**. The central La(III) ion is nona-coordinated by one bromine anion, two chlorine anions, two chelate carboxylates and two monodentate carboxylates, respectively, from four nip ligands in a capped square antiprism environment. The bond lengths of La–O, La–Cl and La–Br are 2.496(7)–2.733(8) Å, 2.848(3)–2.877(3) Å, and 2.943(2) Å, within the expected ranges reported for La(III) complexes.[13]

Crystal structure analysis reveals that **2** exhibits a layered anionic framework consisting of 1D chains similar to that in **1**. In contrast to the La(III)–Co(II) chains in **1**, the 1D chains in **2** are composed entirely of La(III) ions, connected by chlorine anions and carboxylate oxygens of nip ligands as shown in Fig. 3a. The nip ligand connects adjacent 1D chains through its one carboxylate bridging two La(III) ions from one neighboring chain in chelating/bridging mode, and another carboxylate also bridging two La(III) ions from another neighboring chain in the same coordination mode, producing a 2D network as shown in Fig. 3b. The void space of the 2D anionic network is occupied by the EMIm cations. Significantly, all chains in **2** running along a crystallographic 2_1 screw axis in the *c* direction, exhibit the same left-hand helicity and lead to the non-center 2D network. To the best of our knowledge, **2** is the first Ln(III)-based coordination polymer entirely consisting of Ln(III) ion reported through ionothermal synthesis on the survey of Cambridge Database.[14] It was mentioned that, owing to ionothermal reaction effectively preventing the coordination of water from La(III) ion, the structure of **2** is much different from that obtained from hydrothermal synthesis, despite the same organic ligand employed.[15]

Thermogravimetric analysis shows that compound **1** has no weight loss before 265 °C in air (see Fig. S1†). Between 265 and 435 °C, compound **1** undergoes weight loss in two steps. The first weight loss covered a temperature range from 265 to 435 °C, the weight loss of 40.3% corresponds to loss of EMIm cations and mipt ligands (41.2%). The second weight loss covered a temperature range from 435 to 600 °C, the weight loss of 15.4% corresponds to the removal of the CH_3COO^- ligands and the $CH_3SO_3^-$ ligands. Thermogravimetric analyses shows that compound **2** has no weight loss before 280 °C (see Fig S2†). The organic contents begin to be lost in continuous steps until about 550 °C. The total weight loss of 62.8% corresponds to the loss of the EMIm cations, the chlorine and the nip ligands (calcd 62.2%).

In summary, we have reported two lanthanide-involved layered anionic metal–organic frameworks synthesized through ionothermal reaction. We reveal that the structure of the Ln(III)-based coordination polymer obtained from ionothermal synthesis often exhibits different structural patterns from those obtained using a routine synthetic approach, due to lacking of the coordination of water (or solvent) to Ln(III) center. Thus, the present work demonstrates that ionothermal synthesis is an efficient synthetic approach to new lanthanide-based coordination materials.

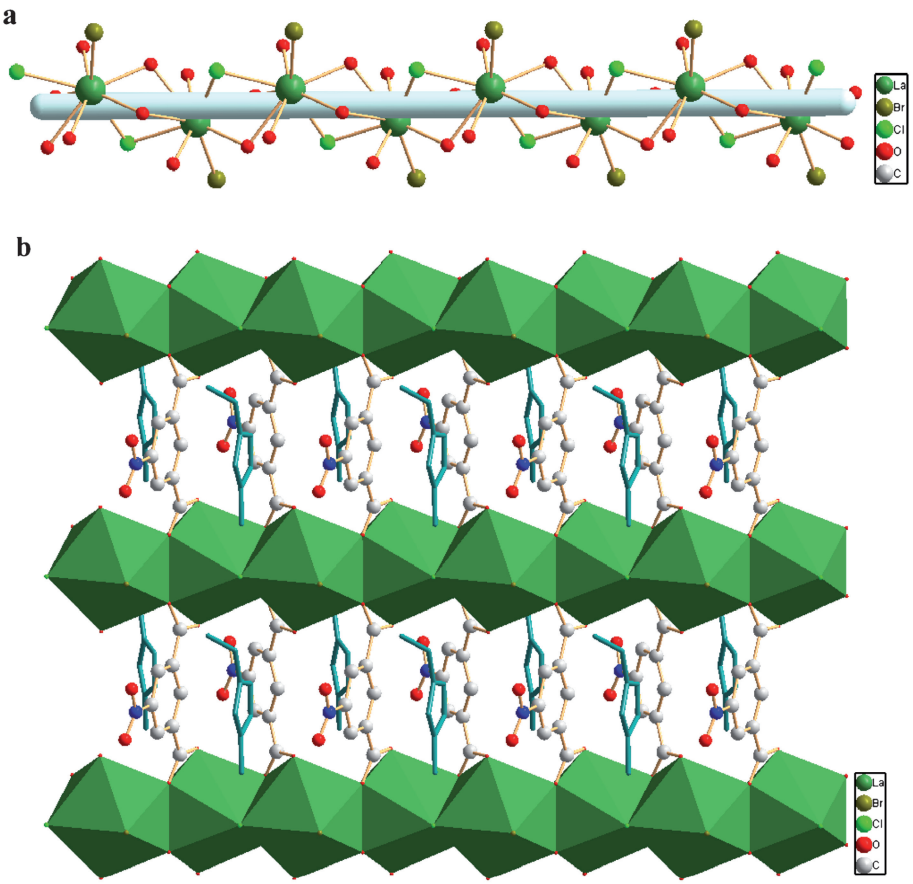

Fig. 3 (a) Ball and stick plot showing the 1D chain structure in **2**. (b) Polyhedral view of the 2D structure of **2**.

Acknowledgements

We thank the NNSFC (Grant Nos. 20825103 and 20721001), the 973 project (Grant 2007CB815304) from MSTC and the Natural Science Foundation of the Fujian Province of China (Grant No. 2008J0010) for financial support.

Notes and references

‡ Compound **1** was synthesized as follows: 0.353 g $LaCl_3 \cdot nH_2O$, 0.249 g $Co(OOCCH_3)_2 \cdot 4H_2O$ and 0.180 g 5-methylisophthalic acid were mixed in 1.3 mL 1-ethyl-3-methyl imidazolium methanesulfonate. Then the mixture was subsequently sealed to a 25 mL Teflon-lined Parr at 160 °C for about a week and cooled to room temperature at the rate of 3 °C h^{-1}. The pink crystals were obtained with 21.7% yield (based on $LaCl_3 \cdot nH_2O$). Anal. Calcd. (Found) for $C_{38}H_{52}N_4O_{24}S_4La_2Co$ (**1**): C, 32.25(32.00); N, 3.96(3.66); H, 3.68(3.82). IR Spectra for **1** (KBr, cm^{-1}): 3423.94(s), 1611.85(s), 1541.73(s), 1433.74.(s), 1380.93(s), 1240.05(s), 1172.34(s), 1047.27(s), 3102.87(m), 550.04(m), 782.87(m), 848.70(w), 724.63(w), 524.96(w).

Compound **2** was ionothermal synthesized as follows: a mixture of 0.353 g $LaCl_3 \cdot nH_2O$, 0.211 g 5-nitroisophthalic acid and 1.2 g ionic liquid 1-ethyl-3-methyl imidazolium bromide was sealed to a 25 mL Teflon-lined Parr at 140 °C for about a week and then cooled to room temperature at the rate of 3 °C h^{-1}. The colorless crystals were obtained with 30.4% yield (based on $LaCl_3 \cdot nH_2O$). Anal. Calcd. (Found) for $C_{14}H_{14}N_3O_6ClBrLa$ (**2**): C, 29.24(29.21); N, 7.31(7.21); H, 2.44(2.83). IR Spectra for **2** (KBr, cm^{-1}): 3432.22(s), 1620.55(s), 1543.10(s), 1382.38(s), 1455.15(s), 3051.33(m), 1349.72(m), 1165.54(m), 725.17(m), 1090.77(w), 790.99(w), 524.02(w).

§ Crystal data for **1**: formula $La_2CoC_{38}H_{52}O_{24}N_4S_4$, M_r = 1413.83, triclinic, space group $P\bar{1}$, a = 10.444(2) Å, b = 11.213(2) Å, c = 12.233(2) Å, α = 79.66 (3)°, β = 71.61 (3)°, γ = 87.54 (3)°, V = 1337.2(5) $Å^3$, Z = 1, ρ_{calcd} = 1.756 g cm^{-3}. Of the 11611 reflections collected, 5238 are independent (R_{int} = 0.0375) and 4749 are observed ($I > 2\sigma(I)$). There is the highest residual peak (2.692), locating at about 1.02 Å around Co atom in **1**. On the basis of all these data and 334 refined parameters, R_1(obs.) = 0.0426 and wR_2(all data) = 0.1255 were obtained.

Crystal data for **2**: formula $LaC_{14}H_{14}O_6N_3BrCl$, M_r = 574.55, orthorhombic, space group $Pca2_1$, a = 24.509(6) Å, b = 9.835(2) Å, c = 7.5626(19) Å, V = 1822.8(8) $Å^3$, Z = 4, ρ_{calcd} = 2.094 g cm^{-3}, Flack parameter 0.30(3), indicating that crystal **2** is a racemic twinning with two enantiomorphs in a ratio of 0.3 : 0.7. There are 7 restraints in the refinement of **2**, which is generated by using the instruction of ISOR 0.01 for the C8 atom in the organic ligand. If the instruction was not used, the refinement of **2** would result in C8 atom non-positive definition. There is the highest residual peak (4.94), locating at about 1.29 Å around La atom in **2**. The 8 H atoms associated with the mutual disorder of the ethyl and methyl C atoms were refined as follows: C12: This has two unit-occupancy H atoms H12A and H12B and one half-occupancy H atom H12C (which lies along the C12–C15 bond); C13: This ha two unit-occupancy H atoms H13A and H13B and one half-occupancy H atom H13C (which lies along the C13–C14 bond); C14 and C15: These have a half-occupancy and should each have three half-occupancy H atoms. Of the 9639 reflections collected, 3430 are independent (R_{int} = 0.0539) and 3006 are observed ($I > 2\sigma(I)$). On the basis of all these data and 245 refined parameters, R_1(obs.) = 0.0546 and wR_2(all data) = 0.1380 were obtained. CCDC nos. of 717557 and 717558 for **1** and **2**, respectively.

1 (*a*) R. D. Rogers and K. R. Seddon, *Science*, 2003, **302**, 792; (*b*) K. E. Gutowski, G. A. Broker, H. D. Willauer, J. G. Huddleston, R. P. Swatloski, J. D. Holbrey and R. D. Rogers, *J. Am. Chem.*

Soc., 2003, **125**, 6632; (*c*) R. Ludwig and U. Kragl, *Angew. Chem., Int. Ed.*, 2007, **46**, 6582.
2 J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156.
3 (*a*) J. G. Huddleston, H. D. Willauer, R. P. Swatloski, A. E. Visser and R. D. Rogers, *Chem. Commun.*, 1998, 1765; (*b*) T. Welton, *Chem. Rev.*, 1999, **99**, 2071; (*c*) E. Dickinson, M. E. Williams, S. M. Hendrickson, H. Masui and R. W. Murray, *J. Am. Chem. Soc.*, 1999, **121**, 613.
4 (*a*) E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald and R. E. Morris, *Nature*, 2004, **430**, 1012; (*b*) E. R. Parnham, P. S. Wheatley and R. E. Morris, *Chem. Commun.*, 2006, 380; (*c*) E. R. Parnham and R. E. Morris, *J. Am. Chem. Soc.*, 2006, **128**, 2204; (*d*) E. R. Parnham and R. E. Morris, *Chem. Mater.*, 2006, **18**, 4882; (*e*) E. A. Drylie, D. S. Wragg, E. R. Parnham, P. S. Wheatley, A. M. Z. Slawin, J. E. Warren and R. E. Morris, *Angew. Chem., Int. Ed.*, 2007, **46**, 7839.
5 (*a*) K. Jin, X. Huang, L. Pang, J. Li, A. Appel and S. Wherland, *Chem. Commun.*, 2002, 2872; (*b*) W. M. Reichert, J. D. Holbrey, K. B. Vigour, T. D. Morgan, G. A. Broker and R. D. Rogers, *Chem. Commun.*, 2006, 4767; (*c*) E. R. Parnham and R. E. Morris, *Acc. Chem. Res.*, 2007, **40**, 1005.
6 (*a*) Y. P. Ren, X. J. Kong, X. Y. Hu, M. Sun, L. S. Long, R. B. Huang and L. S. Zheng, *Inorg. Chem.*, 2006, **45**, 4016; (*b*) A. Demessence, G. Rogez, R. Welter and P. Rabu, *Inorg. Chem.*, 2007, **46**, 3423; (*c*) R. Q. Zou, H. Sakurai, S. Han, R. Q. Zhong and Q. Xu, *J. Am. Chem. Soc.*, 2007, **129**, 8402.
7 (*a*) S. Ma, D. Sun, X. S. Wang and H. C. Zhou, *Angew. Chem., Int. Ed.*, 2007, **46**, 2458; (*b*) W. X. Chen, S. T. Wu, L. S. Long, R. B. Huang and L. S. Zheng, *Cryst. Growth Des.*, 2007, **7**, 1171; (*c*) X. N. Cheng, W. Xue, W. X. Zhang and X. M. Chen, *Chem. Mater.*, 2008, **20**, 5345.
8 (*a*) Z. Lin, D. S. Wragg and R. E. Morris, *Chem. Commun.*, 2006, 2021; (*b*) Z. Lin, A. M. Z. Slawin and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 4880; (*c*) Z. Lin, D. S. Wragg, J. E. Warren and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 10334; (*d*) S. Chen, J. Zhang and X. Bu, *Inorg. Chem.*, 2008, **47**, 5567.
9 (*a*) J. H. Liao, P. C. Wu and W. C. Huang, *Cryst. Growth Des.*, 2006, **6**, 1062; (*b*) J. H. Liao and W. C. Huang, *Inorg. Chem. Commun.*, 2006, **9**, 1227; (*c*) L. Xu, E. Y. Choi and Y. U. Kwon, *Inorg. Chem.*, 2007, **46**, 10670; (*d*) L. Xu, E. Y. Choi and Y. U. Kwon, *Inorg. Chem.*, 2008, **47**, 1907.
10 (*a*) H. J. Eppley and A. Sarkissian, *227th National Meeting of the American Chemical Society, Anaheim, California*, American Chemical Society, Washington, D.C., 2004, 442; (*b*) C. C. Hines, D. B. Cordes, S. T. Griffin, S. I. Watts, V. A. Cocalia and R. D. Rogers, *New J. Chem.*, 2008, **32**, 872.
11 E. Tang, Y. M. Dai, J. Zhang, Z. J. Li, Y. G. Yao, J. Zhang and X. D. Huang, *Inorg. Chem.*, 2006, **45**, 6276.
12 Z. H. Zhang, Z. L. Shen, T. Okamura, H. F. Zhu, W. Y. Sun and N. Ueyama, *Cryst. Growth Des.*, 2005, **5**, 1191.
13 (*a*) G. B. Deacon, T. Feng, P. C. Junk, G. Meyer, N. M. Scott, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 2000, **53**, 853; (*b*) S. K. Ghosh and P. K. Bharadwaj, *Inorg. Chem.*, 2004, **43**, 2293; (*c*) U. Baisch, D. B. Dell'Amico, F. Calderazzo, R. Conti, L. Labella, F. Marchetti and E. A. Quadrelli, *Inorg. Chim. Acta*, 2004, **357**, 1538.
14 *Cambridge Structural Database*, version 5.28 updatas; CCDC: Cambridge, UK, August, 2008.
15 S. F. Si, C. H. Li, R. L. Wang and Y. D. Li, *J. Mol. Struct.*, 2004, **703**, 11.